# Anomalous transmission through heavily doped conducting polymer films with periodic subwavelength hole array

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## ABSTRACT

We observed resonantly enhanced (or anomalous transmission) terahertz transmission through two-dimensional (2D) periodic arrays of subwavelength apertures with various periodicities fabricated on metallic organic conducting polymer films of polypyrrole heavily doped with $PF_6$ molecules [PPy(PF6)]. The anomalous transmission spectra are in good agreement with a model involving surface plasmon polariton excitations on the film surfaces. We also found that the resonantly enhanced transmission peaks are broader in the exotic metallic PPy(PF6) films compared to those formed in 2D aperture array in regular metallic films such as silver, indicating that the surface plasmon polaritons on the PPy(PF6) film surfaces have higher attenuation.

Keywords: Surface plasmon polaritons, resonantly enhanced transmission, anomalous transmission, 2D subwavelength hole array, conducting polymers, terahertz time-domain spectroscopy.

## 1. INTRODUCTION

Since Ebbesen *et al.* reported the phenomenon of "anomalous transmission" through optically thick metallic films perforated with two-dimensional (2D) subwavelength hole arrays,[1] numerous studies have been carried out to explore both fundamental issues and potential device applications.[1-10] In pursuing these goals, there has been significant interest in expanding the range of experimental conditions under which this phenomenon may be observed. For example, whereas much of the early work in this area focused on studies at optical frequencies, there have been several recent demonstrations reporting observations of enhanced transmission at mid-infrared[3], terahertz (THz)[4-8], and microwave frequencies[9]. Over this broad range of the electromagnetic (EM) spectrum, arrays fabricated on metal films have been the most intensely investigated. 2D periodic structures in such films not only allow for reasonable coupling of freely propagating radiation to surface EM waves, or surface plasmon polaritons (SPP) but also exhibit attenuation properties for these surface modes that are perceived as adequate. The attenuation length is particularly long in the THz and microwave EM spectral ranges. Recent materials in which the phenomenon of "anomalous transmission" through 2D aperture arrays has been demonstrated include amorphous silicon at optical frequencies[10], and semiconductors at THz frequencies[4].

Here we report, for the first time the observation of "anomalous transmission" in 2D hole arrays perforated on films of another, more exotic class of conductors, namely heavily-doped conducting polymers[11]. Doped conducting polymers such as polyacetylene, polyaniline and polypyrrole, show a metal-insulator transition at high doping levels of a few percent.[12] Among the class of conducting polymers, polypyrrole [PPy] heavily-doped with $PF_6$ [PPy(PF6)] is one of the highly conducting polymer, with very good stability in air.[12-15] Also its conductivity is large (> 100 S/cm) even at cryogenic temperatures. It has been postulated that heavily doped PPy(PF6) films have two plasma frequencies, where the lower frequency is caused by a Drude free carrier dielectric response with a plasma frequency in the THz spectral range. Our findings show that SPP excitations can be formed on the surfaces of metallic conducting polymers; so in this sense these novel organic metallic films behave like regular metals. However when comparing the "anomalous transmission" spectra of the heavily doped polymer films with those of regular metals such as Ag, we found that the

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SPP in PPy(PF6) have much larger attenuation. Furthermore we also found that the resonantly enhanced transmission spectrum in the polymer films diminishes much faster than the DC electrical conductivity at low doping levels.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

The PPy films (see Fig. 1 inset for the polymer unit) were polymerized and doped electrochemically with $PF_6$ molecules at –40°C. From earlier studies[13] it is known that in fully doped films there exists one dopant $PF_6$ ion for every four PPy monomers in the polymer chain. We measured in our most heavily doped films the room-temperature DC conductivity to be ~ 200 S/cm. For obtaining the 2D aperture array, the PPy(PF6) films were peeled off the electrodes following polymerization yielding free-standing films with thicknesses of ~ 25 μm. The 2D hole arrays were fabricated on the polymer films using a pulsed excimer laser machining system (Optec, MicroMaster) in a square lattice geometry. We fabricated two samples with different periodicities of 1 mm and 1.5 mm, respectively on the most heavily doped PPy(PF6) film, with a corresponding hole diameter of 0.5 mm and 0.75 mm, respectively. The fractional aperture area was thus ~ 20 %. Hole arrays on other, less heavily doped films were also studied.

### 2.2 Terahertz time-domain spectroscopy measurements

We first measured the complex dielectric constant spectrum of the unperforated PPy(PF6) film in the THz EM range and then examined the transmission characteristics of 2D periodic subwavelength aperture arrays fabricated on the PPy(PF6) films using conventional THz time-domain spectroscopy (THz-TDS).[16] In our setup, photoconductive (PC) devices were used for both THz generation and coherent detection. The sample was placed at the center of two off-axis parabolic mirrors used to collect, collimate, and focus the THz EM radiation. The THz EM beam was normally incident on the film surface and linearly polarized. Reference spectra were measured without the sample for normalization purposes. A unique feature of the THz-TDS technique is that it allows for a direct measurement of the THz electric field, so that both amplitude and phase information are obtained simultaneously. By Fourier-transforming the ps time-resolved PC data into the frequency-domain, we can then obtain both real ($n_r$) and imaginary ($\kappa$) THz refractive indices from the resulting magnitude and phase spectra directly, without the need for Kramers-Kronig analysis. Using this information, we obtained the real and imaginary dielectric constants from $\varepsilon = \varepsilon' + i\varepsilon'' = n^2 = (n_r + i\kappa)^2$ (here $\varepsilon$ and $n = n_r + i\kappa$ are the complex dielectric constant and complex refractive index, respectively).

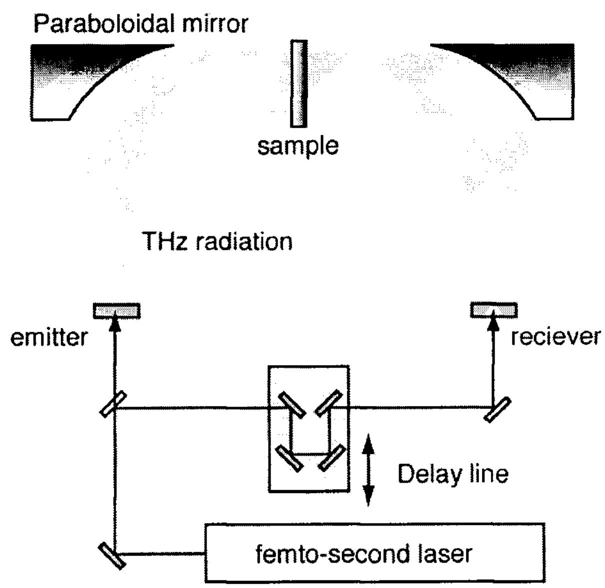


Fig.1 Schematic representation of the optical setup for the THz-TDS measurements.

## 3. RESULTS AND DISCUSSION

### 3.1 Dielectric constants of PPy(PF6)

Figure 2 shows the measured real ($\varepsilon'$) and imaginary ($\varepsilon''$) dielectric constant spectra of the most heavily doped PPy(PF6) film in the THz spectral range relevant to the resonant transmission measurements discussed below. We indeed found that ε' is negative over the spectral range of interest, and this corresponds to 'metallic' behavior. Thus the PPy(PF6) film should support SPP excitations. Our obtained dielectric spectra are consistent with those of Martens *et al.*[17] who found that the dielectric function of PPy(PF6) films is consistent with a Drude free carrier response with a very short scattering time of order 10 fs; we thus expect the SPP attenuation in such films to be relatively high.

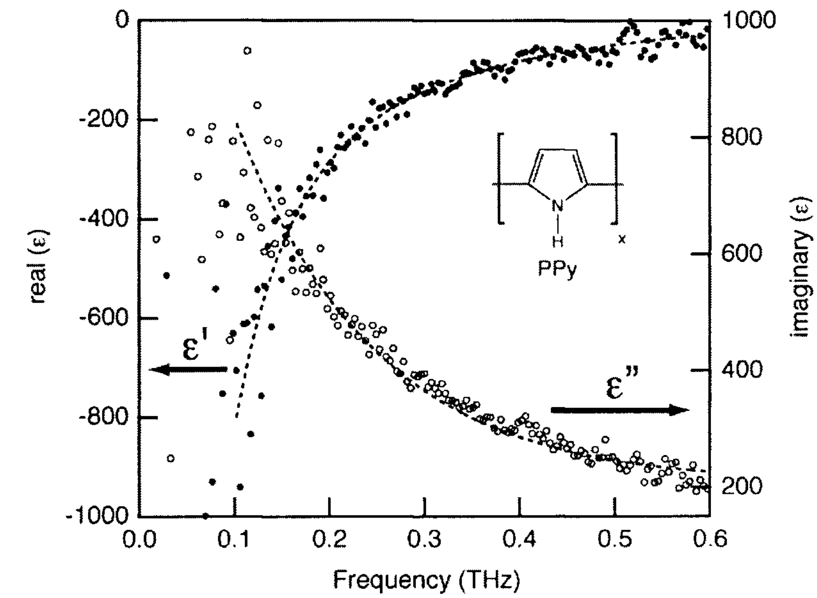


Fig. 2: Spectra of the real (ε'; filled circles) and imaginary (ε"; empty circles) components of the dielectric constant in the THz spectral range for the most heavily doped PPy(PF6) free standing 25 μm thick film. The lines are guide to the eye. Inset: molecular structure of the PPy polymer.

### 3.2 Transmission spectra through aperture array on PPy(PF6) film

The optical transmission characteristics of the two hole arrays polymer films were measured using the THz-TDS technique discussed above. The polarization of the incident THz beam was parallel to the aperture rows, with the detector oriented to measure the same polarization. Figure 3 shows a typical transient response of THz radiation through the perforated film, and also for reference the transient transmission without any sample, for normalization purpose. The transient response data were used to calculate the absolute amplitude transmission coefficient as a function of frequency, as explained above.

Figure 4 shows the Fourier-transformed frequency-domain transmission spectra through the free-standing heavily doped PPy(PF6) film perforated with hole array of 1 mm (full line) and 1.5 mm (dotted line) periodicities, respectively. The transmission spectrum for the unperforated film is also shown (dashed line) for comparison. It is seen that without the perforated hole array, the 25 μm thick PPy(PF6) film is nearly opaque. However, when the hole array is fabricated on the film, resonantly enhanced transmission peaks are observed in the spectra. For the sample with 1 mm periodicity at the peak frequency of 0.27 THz, the transmittance is almost 60 %. This is much larger than the fractional aperture area (~ 20 %), and this indicates that anomalously enhanced transmission was obtained.

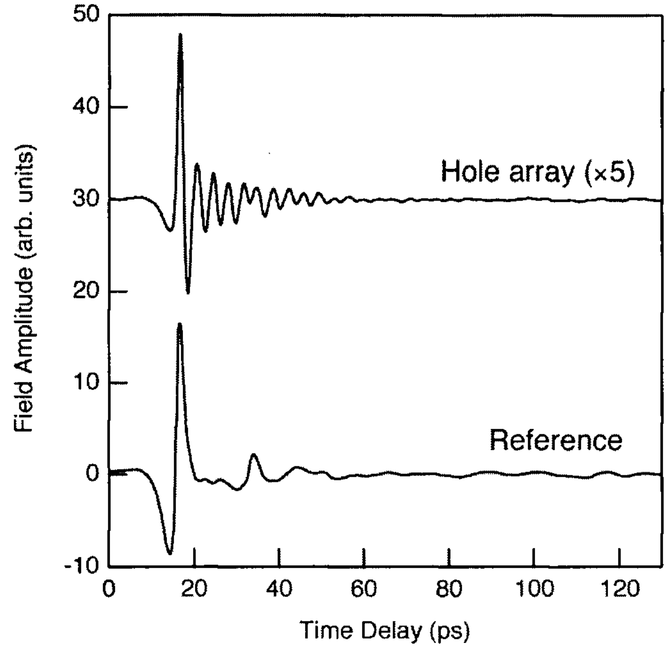


Fig. 3: THz time-domain waveforms transmitted through the heavily doped free-standing PPy(PF6) film perforated with two-dimensional hole array, and in the absence of the sample, for reference.

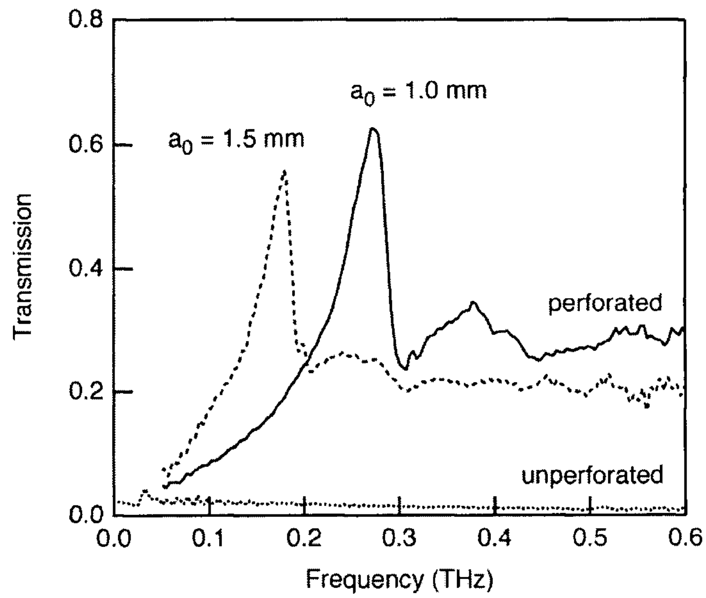


Fig. 4: Frequency-domain transmission spectra of two heavily doped free-standing PPy(PF6) films with 1 mm (solid trace) and 1.5 mm (dashed trace) periodicity, as well as for an unperforated film (dotted trace).

The resonantly enhanced transmission peaks, $\lambda_{SPP}$ agree with the conventionally used model for such structures. In this model, the SPP dispersion relation for a perforated film is approximated by the dispersion relation of an unperforated film, which is expressed as[18]

$$\lambda_{SPP} = \frac{a_0}{\sqrt{i^2 + j^2}} \left( \frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \right)^{1/2}, \tag{1}$$

where $\varepsilon_m$ and $\varepsilon_d$ are the dielectric constants of the metal (i.e., PPy(PF6)) and the dielectrics surrounding the metal (i.e., air), $a_0$ is the hole array lattice constant, and $i$ and $j$ are integers denoting the diffraction order. For the 1 mm 2D periodicity two prominent transmission peaks and another that is less prominent may be identified. The transmission peaks for the 1 mm periodicity occur at $\nu_1 = 0.27$ THz; $\nu_2 = 0.38$ THz; and $\nu_3 = 0.55$ THz, which correspond to $\lambda_1 = 1.11$ mm; $\lambda_2 = 0.79$ mm; and $\lambda_3 = 0.55$ mm, respectively. These wavelength values are in excellent agreement relative to each other when calculating $\lambda$'s using Eq.(1) for $(i, j) = (\pm 1, 0), (\pm 1, \pm 1)$, and $(\pm 2, 0)$, respectively. Also their absolute values is in fair agreement with Eq.(1) using the dielectric response given in Fig. 2. We therefore conclude that these anomalous transmission peaks are related to resonant interactions with SPP.

By changing the periodicity of the 2D hole array to 1.5 mm, the transmission peaks shift to a correspondingly lower frequency (dashed line in Fig.4). Resonantly enhanced transmission peaks are now observed at $\nu_1 = 0.18$ THz and $\nu_2 = 0.25$ THz; no other transmission peak can be identified for this film. The resonant transmission bands are at $\lambda_1 = 1.67$ mm and $\lambda_2 = 1.20$ mm, respectively. These wavelengths agree very well with the new periodicity using Eq.(1) when taking into account an increase factor of 1.5 in the lattice constant periodicity $a_0$. We therefore conclude that this simple, commonly used model can adequately explain our experimental observations. Our results indicate that heavily doped conducting polymers contain large density of "free carriers" that allow direct excitation of SPP similar to normal metals, in spite of the known intrinsically disordered quasi-one dimensional character of these materials.

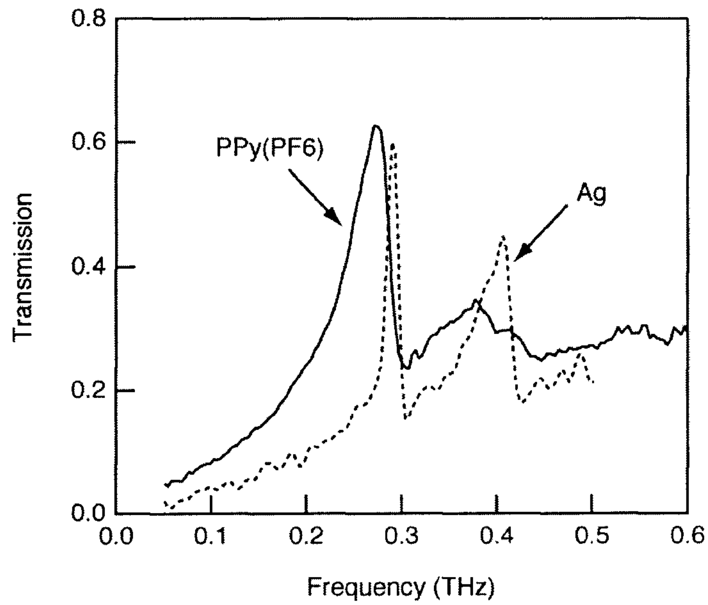


Fig. 5: THz transmission spectra through the free-standing heavily doped PPy(PF6) film with 1 mm periodicity (solid trace) and a stainless steel foil over-coated with Ag (dotted trace) having the same periodicity

In Fig. 5 we compare the anomalous transmission spectra of the heavily doped film to that obtained on a stainless steel film having the same periodicity. Both films show anomalous transmission that contains resonant peaks as well as anti-resonances (AR) at their higher frequency side. We note that the bandwidth of the lowest order transmission peak in the PPy(PF6) spectrum is much broader than the corresponding peak in the regular metallic films.[11] Although the transmission peaks have roughly the same value (~60%) in both samples, nevertheless the lowest order [namely (±1, 0)] resonant peak in the polymer film is broader by a factor of ~3 compared to the corresponding width of the corresponding band in the Ag film. In addition the [1,0] frequency in the polymer film is red-shifted compared to that in the Ag film. We attribute the broader transmission resonance band for the PPy(PF6) sample to the fact that SPP excitations experience greater propagation losses in the doped conducting polymer compared to that in the metal film. The reason for the red-shifted resonance in the perforated PPy(PF6) film compared to the Ag film is less clear. On the contrary we note that the AR frequencies occur *at the same frequencies* in both films. This may indicate that the AR spectral features are much closely related to the lattice periodicity than the enhanced transmission peaks. In fact the AR frequencies fit much better Eq.(1) than the transmission peaks. For example the AR that is related to the [1,0] transmission band occurs at ~ 3 THz that corresponds to 1 mm if we take an effective refraction index, $n_{eff} = 1$; this fits exactly Eq. (1). We thus conclude that the AR features in the transmission spectrum play an important role understanding the "anomalous transmission" phenomenon.

The polymer film electrical conductivity may be controlled *in situ* by changing the doping level using an electrochemical technique. This may allow to tune the transmission characteristics of the perforated doped films simply by applying an external voltage in the electrochemical cell. With this goal in mind we fabricated hole arrays on conducting polymer films of various doping levels, and measured the 'anomalous transmission' spectra as shown in Fig.6. For ease of comparison the value of the lattice constant periodicity of these perforated films was kept constant at $a_0 = 1.0$ mm, and the diameter of the holes was also kept constant at 0.4 mm, so that the fractional aperture area was ~ 12 % for all films. For the highest conductivity (345 S/cm) film, sharp [1,0] peak with transmission value of ~ 60% was observed at ~ 0.27 THz. At lower conductivity (214 S/cm) the transmission peak became less prominent; and when

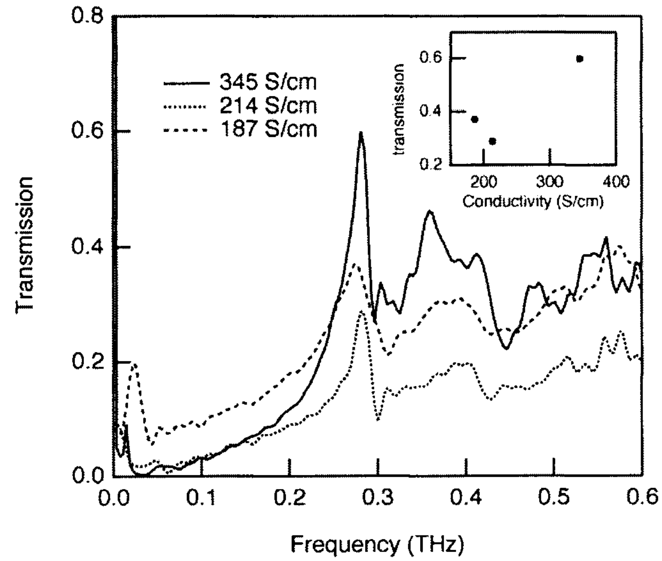


Fig. 6: Anomalous transmission spectra for three perforated free-standing PPy(PF6) films of various doping levels as deduced from their DC electrical conductivities: 345 S/cm (solid trace), 214 S/cm (dotted trace) and 187 (dashed trace); the hole array periodicity and hole diameter were kept constant at 1 mm and 0.4 mm, respectfully. The inset shows the value of the [1,0] transmission maximum as a function of the film conductivity.

conductivity is less than 187 S/cm the PPy(PF6) film became semi-transparent and thus the resonantly enhanced band is much weaker. We believe that these results are promising to realize tunable plasmonic lattices by *in situ* tuning of doping level of PPy(PF6) films. This *in situ* tuning project is currently under study.

## 4. CONCLUSIONS

In conclusion, we studied "anomalous transmission" through heavily doped organic conducting polymer PPy(PF6) films that were perforated with 2D subwavelength hole array with various periodicities. The resonance transmission bands and the corresponding anti-resonances are in good agreement with a model of SPP excitations on the perforated films. Using organic conducting polymers of which properties may be widely varied by electro-chemical means, we would be able to fabricate a variety of novel optical devices that may not be possible using more usual metallic films. Moreover, it is also conceivable that using the phenomenon of "anomalous transmission" as a spectroscopic technique we would be able to better understand the doping process and transport mechanism in heavily-doped conducting polymer. These topics are still being actively debated in the field.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, "Extraordinary optical transmission through sub-wavelength hole arrays," Nature (London) **391**, 667-669 (1998).
2. H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen, and H. J. Lezec, "Surface plasmons enhance optical transmission through subwavelength holes," Phys. Rev. B **58**, 6779-6782 (1998).
3. Y.-H. Ye and J.-Y. Zhang, "Middle-infrared transmission enhancement through periodically perforated metal films," Appl. Phys. Lett. **84**, 2977-2979 (2004).
4. J. G. Rivas, C. Schotsch, P. H. Bolivar, and H. Kurz, "Enhanced transmission of THz radiation through subwavelength holes," Phys. Rev. B **68**, R201306 (2003).
5. H. Cao and A. Nahata, "Resonantly enhanced transmission of terahertz radiation through a periodic array of subwavelength apertures," Opt. Express **12**, 1004-1010 (2004).
6. D. Qu, D. Grischkowsky, and W. Zhang, "Terahertz transmission properties of thin, subwavelength metallic hole arrays," Opt. Lett. **29**, 896-898 (2004).
7. F. Miyamaru and M. Hangyo, "Finite size effect of transmission property for metal hole arrays in subterahertz region," Appl. Phys. Lett. 84, 2742-2744 (2004).
8. H. Cao and A. Nahata, "Influence of aperture shape on the transmission properties of a periodic array of subwavelength apertures," Opt. Express **12**, 3664-3672 (2004).
9. M. Beruete, M. Sorolla, I. Campillo, J.S. Dolado, L. Martin-Moreno, J. Bravo-Abad, and F.J. Garcia Vidal, "Enhanced millimeter-wave transmission through subwavelength hole arrays," Opt. Lett. **29**, 2500-2502 (2004).
10. H. J. Lezec and T. Thio, "Diffracted evanescent wave model for enhanced and suppressed optical transmission through subwavelength hole arrays," Opt. Express **12**, 3629-3651 (2004).
11. T. Matsui, Z. V. Vardeny, A. Agrawal, A. Nahata, and R. Menon, "Resonantly-enhanced transmission through a periodic array of subwavelength apertures in heavily-doped conducting polymer films," Appl. Phys. Lett. **88**, 071101 (2006).
12. R. Menon, C. O. Yoon, D. Moses, and A. J. Heeger, "Metal-Insulator Transition in Doped Conducting Polymer," *Handbook of Conducting Polymers*, edited by T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, 27-84, Marcel Dekker, New York, 1998.
13. C. O. Yoon, R. Menon, D. Moses, and A. J. Heeger, "Transport near metal-insulator transition: Polypyrrole doped with PF6," Phys. Rev. B **49**, 10851-10863 (1994).

14. K. Lee, R. Menon, C. O. Yoon, and A. J. Heeger, "Reflectance of conducting polypyrrole: Observation of the metal-insulator transition driven by disorder," Phys. Rev. B **52**, 4779-4787 (1995).
15. R. S. Kohlman, J. Joo, Y. Z. Wang, J. P. Pouget, H. Kaneko, T. Ishiguro, and A. J. Epstein, "Drude metallic response of polypyrrole," Phys. Rev. Lett. **74**, 773-776 (1995).
16. D. Grischkowsky, "Nonlinear generation of sub-psec pulses of THz electromagnetic radiation by optoelectronics – applications to time-domain spectroscopy", *Frontiers in Nonlinear Optics*, H. Walther, N. Koroteev, and M. O. Scully eds. 196-227, Institute of Physics Publishing, Philadelphia, 1992.
17. H. C. F. Martens, J. A. Reedijk, H. B. Brom, D. M. de Leeuw, and R. Menon, "Metallic state in disordered quasi-one-dimensional conductors," Phys. Rev. B **63**, 073203 (2001).
18. H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* Springer, Berlin, 1988.